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DERWENT-WEEK: 200313

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TITLE: Coating agent for coating on thermoplastic resin film,
contains vinyl polymer having vinyl alcohol unit,
olefin-maleic acid copolymer having maleic acid or
anhydride units and inorganic layered compound

PATENT-ASSIGNEE: UNITIKA LTD[NIRA]

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PATENT-FAMILY:

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ABSTRACTED-PUB-NO: JP2001335736A

BASIC-ABSTRACT:

NOVELTY - The coating agent is an aqueous solution containing (in mole%) vinyl polymer having vinyl alcohol units (40 or more), an olefin-maleic acid copolymer having maleic acid or anhydride units (10 or more) and an inorganic layered compound. The weight ratio of the vinyl polymer to the olefin-maleic acid copolymer is 97/3-20/80. The total of vinyl polymer and the copolymer to the inorganic compound is 10000/1-1/2.

USE - For coating on thermoplastic resin film.

ADVANTAGE - The coating agent forms a coating layer having excellent gas barrier property even in high humid conditions.

CHOSEN-DRAWING: Dwg.1/1

TITLE-TERMS: COATING AGENT COATING THERMOPLASTIC RESIN FILM CONTAIN VINYL

POLYMER VINYL ALCOHOL UNIT OLEFIN MALEIC ACID COPOLYMER MALEIC ACID

ANHYDRIDE UNIT INORGANIC LAYER COMPOUND

DERWENT-CLASS: A14 A17 A82 G02 P73

CPI-CODES: A04-F05; A07-A02C; A10-E09B1; A12-B01E; A12-B01G; G02-A02C;

G02-A02D;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; H0317 ; S9999 S1285*R

Polymer Index [1.2]

018 ; ND01 ; K9676*R ; K9687 K9676 ; K9712 K9676 ; K9574 K9483

Polymer Index [1.3]

018 ; B9999 B5447 B5414 B5403 B5276

Polymer Index [2.1]

018 ; G0033*R G0022 D01 D02 D51 D53 ; R00843 G0760 G0022 D01 D23 D22 D31 D42 D51 D53 D59 D65 D75 D84 F39 E00 E01 ; H0011*R ;

P1694*R

D01 ; S9999 S1616 S1605 ; H0011*R ; P1150

Polymer Index [2.2]

018 ; G0033*R G0022 D01 D02 D51 D53 ; R00901 G0760 G0022 D01 D12 D10 D51 D53 D59 D60 D84 F37 F35 E00 E01 ; H0011*R ; P1694*R D01 ; S9999 S1616 S1605 ; H0011*R ; P1150

Polymer Index [2.3]

018 ; ND01 ; K9676*R ; K9687 K9676 ; K9712 K9676 ; K9574 K9483

Polymer Index [2.4]

018 ; K9745*R ; Q9999 Q7114*R ; Q9999 Q6780 ; B9999 B4864 B4853 B4740

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C2003-033901

Non-CPI Secondary Accession Numbers: N2003-104638

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the gas barrier property film which formed at least in one side of a thermoplastics film the gas barrier property coat agent and it which have the gas barrier property excellent also in the bottom of high humidity.

[0002]

[Description of the Prior Art] Since thermoplastics films, such as a polyamide and polyester, are excellent in reinforcement, transparency, a moldability, and gas barrier property, they are used for the application broad as wrapping. However, when using for the application asked for prolonged shelf lives, such as retorting food, still more advanced gas barrier property is required.

[0003] In order to improve gas barrier property, the film which carried out the laminating of the polyvinylidene chloride (PVDC) to the front face of these thermoplastics films has been broadly used for food packing etc., but since PVDC generates organic substances, such as a sour gas, at the time of incineration, while the interest about an environment increases in recent years, shift to other ingredients is desired strongly.

[0004] Although polyvinyl alcohol (PVA) does not have generating of a toxic gas, either and the gas barrier property under a low humidity ambient atmosphere is also high as an ingredient which changes to PVDC, gas barrier property cannot fall rapidly as humidity becomes high, and it cannot use for the package of the food containing moisture etc. in many cases.

[0005] Although the film which consists of a copolymer (EVOH) of vinyl alcohol and ethylene is known as a film which has improved the fall of the gas barrier property under the high humidity of PVA, in order to maintain the gas barrier property under high humidity on practical use level, it is necessary to make the content of ethylene to some extent high. To use EVOH as a coating ingredient, it is required to make it dissolve using the mixed solvent of an organic solvent, or a water and an organic solvent, it is not desirable from a viewpoint of an environmental problem, and since the recovery process of an organic solvent etc. is needed, there is a problem of becoming cost quantity.

[0006] It is widely known by constructing a bridge in PVA using a cross linking agent that the polymer which the deck-watertight-luminaire-ized technique is variously known from the former, for example, contains a maleic-acid unit will react with hydroxyl groups, such as PVA and polysaccharide, and will be deck-watertight-luminaire-ized. For example, having the water resisting property the layer which consists of a 25 - 50% partial neutralization object of an isobutylene-maleic-anhydride copolymer and PVA excelled [water resisting property] in JP,8-66991,A is known. Moreover, the approach of deck-watertight-luminaire-izing the film of PVA is described to JP,49-1649,A by by mixing an alkyl vinyl ether-maleic-anhydride copolymer to PVA.

[0007] However, deck-watertight-luminaire-izing (namely, nonaqueous vitrification) and gas barrier property are different properties, although deck-watertight-luminaire-ized by generally constructing a bridge in a polymer molecule, gas barrier property is a property which prevents invasion and diffusion of oxygen etc. of a comparatively small molecule, even if it only constructs a bridge in a polymer, it

does not restrict that gas barrier property is obtained, for example, as for three-dimensions cross-linking polymers, such as an epoxy resin and phenol resin, it does not have gas barrier property.

[0008] Moreover, although the approach of constructing a bridge by the ester bond in both polymers by carrying out the coat of the water solution which consists of a partial neutralization object of PVA, polyacrylic acid, or polymethacrylic acid to a film, and heat-treating it was proposed (JP,10-237180,A), by this approach, in order to fully advance esterification and to raise the gas barrier property of a film, heating of long duration is required of an elevated temperature, and the problem was in productivity. Since a film colored and an appearance was spoiled by furthermore carrying out a long duration reaction at an elevated temperature, the improvement was required for food packing.

[0009] Moreover, although the approach of denaturalizing carboxyl group content quantity hydrogen bond resin, hydroxyl-group content quantity hydrogen bond nature resin, and the resin constituent that consists of an inorganic sheet silicate with heat and an activity energy line was proposed (JP,10-231434,A), since an activity energy line was needed, the viewpoint of economical efficiency to the further improvement was required.

[0010]

[Problem(s) to be Solved by the Invention] By offering the reactant high barrier property coat agent which raised productivity to the above problems, and applying this coat agent at least to one side of a thermoplastics film, also under high humidity, it has high gas barrier property and, as for this invention persons, coloring also tends to offer few barrier property films.

[0011]

[Means for Solving the Problem] this invention persons reached [that the above-mentioned technical problem is solvable and] header this invention wholeheartedly by applying the coat agent containing a specific resin constituent on the surface of a film, and making the layer which consists of this resin constituent form as a result of research. That is, the summary of this invention is as follows.

(1) a vinyl alcohol unit -- more than 40 mol % -- with the vinyl system polymer (A) to contain In the drainage system coat agent containing the olefin-maleic-acid copolymer (B) to contain and an inorganic stratified compound (C) a maleic acid or a maleic-anhydride unit -- more than 10 mol % -- The gas barrier property coat agent characterized by for the weight ratios of (A) and (B) being $97 / 3 - 20/80$, and being $(A+B)/(C) = 10000 / 1 - 1/2$ (weight ratio).

(2) The gas barrier property film with which the layer which consists of a coat agent of the above-mentioned (1) publication was formed at least in one side of a thermoplastics film.

[0012]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[0013] As a thermoplastics film used in this invention, the layered product of the films which consist of polyolefin resin or those mixture, such as polyester resin, such as polyamide resin, such as nylon 6, Nylon 66, and Nylon 46, polyethylene terephthalate, polyethylenenaphthalate, polybutylene terephthalate, and polybutylene naphthalate, polypropylene, and polyethylene, or those films may be mentioned, and an unstretched film or an oriented film is sufficient.

[0014] As an approach of manufacturing a film, heating fusion of the thermoplastics is carried out with an extruder, it extrudes from a T die, cooling solidification is carried out with a cooling roller etc., an unstretched film is obtained, or extrude from a circular die, it is made to solidify with water cooling or air cooling, and an unstretched film is obtained. When manufacturing an oriented film, once rolling round an unstretched film, the coincidence biaxial extending method or the approach of extending by the biaxial extending method serially is continuously desirable. The approach of combining the flat type producing-film method and the tenter extending method by the T die from a film mechanical property or a thickness homogeneity engine-performance side is desirable.

[0015] Moreover, in order to raise the adhesive property of a film and a coat layer, corona discharge treatment may be carried out to a film front face, or an anchor coat may be carried out.

[0016] The weight ratio of a vinyl system polymer (A) and an olefin-maleic-acid copolymer (B) in this invention needs $97 / 3 - 20/80$, and to be the range of $90 / 10 - 25/75$ preferably. Especially when separating from this range, crosslinking density required in order to make the gas barrier property of the

film under a high humidity ambient atmosphere discover cannot be obtained, and the gas barrier property film made into the purpose of this invention cannot be obtained.

[0017] As for the coat agent in this invention, it is desirable on production that it is water solubility, and since water solubility will be spoiled if a hydrophobic copolymerization component is made to contain so much, it is not desirable. moreover, the vinyl alcohol unit in a vinyl system polymer (A) -- more than 40 mol % -- if to contain is required and this ratio is too low, the rate of an ester ligation reaction with a maleic-acid copolymer (B) cannot fall, and the gas barrier film made into the purpose of this invention cannot be obtained.

[0018] As a typical compound of a vinyl system polymer (A) used in this invention, it is polyvinyl alcohol. Polyvinyl alcohol can obtain the polymer of vinyl ester using completeness or well-known approaches, such as carrying out partial saponification. As vinyl ester, formic acid vinyl, vinyl acetate, propionic-acid vinyl, vinyl pivalate, BASA tic acid vinyl, etc. are mentioned, and vinyl acetate is industrially the most desirable especially.

[0019] The approach of using the alkali saponifying method well-known as the saponification approach and the acid saponifying method, and carrying out alcoholysis in a methanol especially using hydroxylation alkali is desirable. Although whenever [saponification] is so desirable that it is close to 100% from a viewpoint of gas barrier property, there is concern which will be gelled if the temperature of a water solution becomes low, and temperature management is required for preservation. if whenever [saponification] is reduced a little, for example, it is made to about 97% -- the stability of a solution -- markedly -- alike -- increase -- moreover, barrier property ability falls and **** in the water solubility of a polymer, when whenever [saponification] is too low, although there is also almost no fall of barrier property ability -- it is divided. Whenever [desirable saponification] is about 80% or more.

[0020] Next, the olefin-maleic-acid copolymer (B) used in this invention is obtained by carrying out the polymerization of the olefin monomer to a maleic anhydride by well-known approaches, such as a solution radical polymerization. As an olefin monomer which can be copolymerized, the olefin of the carbon numbers 2-30, such as vinyl ester, such as acrylic ester (meta), such as alkyl vinyl ether to the carbon numbers 3-30, such as the methyl vinyl ether and ethyl vinyl ether, a methyl acrylate (meta), an ethyl acrylate (meta), and butyl acrylate (meta), and formic acid vinyl vinyl acetate, styrene, p-styrene sulfonic acid, ethylene, a propylene, and an isobutylene, etc. is mentioned, and such mixture can also be used. Among these, alkyl vinyl ether and low-grade olefins are the most desirable in respect of improvement in gas barrier property.

[0021] the maleic-acid unit in the polymer (B) in this invention -- more than 10 mol % -- to contain is required. If there are few maleic-acid units than ten-mol %, formation of the structure of cross linkage by the reaction with the vinyl alcohol unit in a polymer (A) will be inadequate, and gas barrier property will fall. Moreover, the maleic-acid unit may be esterified or amidated partially.

[0022] In addition, in dryness, the maleic-acid unit in the polymer (B) used by this invention tends to serve as maleic-anhydride structure which the contiguity carboxyl group cyclodehydrated, and in the time of humidity, or a water solution, ring breakage of it is carried out and it serves as maleic-acid structure.

[0023] The inorganic stratified compound in this invention is an inorganic compound which a unit crystal layer laps and forms the layer structure, and swelling and the thing which carries out cleavage are desirable in a solvent.

[0024] As an inorganic stratified compound, a montmorillonite, beidellite, saponite, Hectorite, a sauconite, a vermiculite, a fluorine mica, a muscovite, A palagonite, phlogopite, a biotite, lepidolite, margarite, a klint night, ANANDAITO, chlorite, a DOMBA site, SUDOAITO, KUKKEAITO, Chestnut NOKUROA, a chamosite, Nima Ito, a TETORASHI lyric mica, Talc, pyrophyllite, nacrite, a kaolinite, halloysite, a chrysotile, a sodium TENIO light, xanthophyllite, antigorite, dickite, a hydrotalcite, etc. are mentioned, and a bloating tendency fluorine mica and especially a montmorillonite are desirable.

[0025] It may produce naturally, and these inorganic stratified compounds could compound denaturalize artificially, or may process them with the organic substance, such as an onium salt.

[0026] A bloating tendency fluorine mica system mineral is the most desirable at a point excellent in

transparency, and is shown by the degree type.

$\alpha(\text{MF})$ and $\beta(\text{aMgF}_2 \text{ and } \text{bMgO})$ - γSiO_2 (M expresses sodium or a lithium among a formula, and α , β , γ , a , and b express a multiplier respectively, and are $0.1 \leq \alpha \leq 2$, $2 \leq \beta \leq 3.5$, $3 \leq \gamma \leq 4$, $0 \leq a \leq 1$, $0 \leq b \leq 1$, and $a+b=1$.)

[0027] As a manufacturing method of such a bloating tendency fluorine mica system mineral, oxidation silicon, a magnesium oxide, and various fluorides are mixed, the mixture is fused completely [in a 1400-1500-degree C temperature requirement] all over an electric furnace or a gas furnace, for example, and there is the so-called scorification which carries out crystal growth of the fluorine mica system mineral into a reaction container by the cooling process.

[0028] Moreover, there is a method of carrying out the intercalation of the alkali-metal ion to this, and obtaining a bloating tendency fluorine mica system mineral, using talc as starting material (JP,2-149415,A). By this approach, ** fluoride alkali or fluoride alkali can be mixed to talc, and a bloating tendency fluorine mica system mineral can be obtained by carrying out short-time heat-treatment at about 700-1200 degrees C within a magnetic crucible.

[0029] Under the present circumstances, as for the amount of the ** fluoride alkali mixed with talc, or fluoride alkali, it is desirable to consider as 10 - 35% of the weight of the range of the whole mixture, and since the generation yield of a bloating tendency fluorine mica system mineral falls in separating from this range, it is not desirable.

[0030] The alkali metal of ** fluoride alkali or fluoride alkali has sodium or a desirable lithium. Moreover, in the process which manufactures a bloating tendency fluorine mica system mineral, it is also possible to adjust the bloating tendency of the bloating tendency fluorine mica system mineral which carries out little combination of the alumina and generates it.

[0031] Moreover, in the inorganic stratified compound which can be used in this invention, a montmorillonite is shown by the degree type and can be obtained by refining what is produced naturally.

$\text{MaSi}_4(\text{aluminum}_{2-a}\text{Mg})\text{O}_{10}(\text{OH})_2n\text{H}_2\text{O}$ (M expresses the cation of sodium among a formula and a is 0.25-0.60.) Moreover, since the number of the water molecules combined with the ion-exchange nature cation between layers may change according to conditions, such as a cation kind and humidity, it is expressed with $n\text{H}_2\text{O}$ in a formula. The isomorphism ion substitution product of the MAGUNE cyanogen montmorillonite expressed with degree formula group, an iron montmorillonite, and an iron MAGUNE cyanogen montmorillonite also exists in a montmorillonite again, and these may be used. $\text{MaSi}_4(\text{aluminum}_{1.67-a}\text{Mg}_{0.5+a})\text{O}_{10}(\text{OH})_2$, $n\text{H}_2\text{OMaSi}_4(\text{Fe}_{2-a}\text{Mg}_a)\text{O}_{10}(\text{OH})_2$, and $n\text{H}_2\text{OMaSi}_4(\text{Fe}_{1.67-a}\text{Mg}_{0.5+a})\text{O}_{10}(\text{OH})_2n\text{H}_2\text{O}$ (M expresses the cation of sodium among a formula and a is 0.25-0.60.)

[0032] Usually, although a montmorillonite has ion-exchange nature cations, such as sodium and calcium, between the layer, the content ratio changes with places of production. In this invention, it is desirable that the ion-exchange nature cation between layers is permuted by sodium by ion exchange treatment etc. Moreover, it is desirable to use the montmorillonite refined by elutriation processing.

[0033] Unless the property is spoiled greatly, a thermostabilizer, an antioxidant, reinforcement, a pigment, a degradation inhibitor, a weathering agent, a flame retarder, a plasticizer, a release agent, lubricant, etc. may be added by the resin constituent which constitutes the coat agent in this invention.

[0034] As a thermostabilizer, an antioxidant, and a degradation inhibitor, hindered phenols, phosphorus compounds, hindered amine, a sulfur compound, a copper compound, the halogenides of alkali metal, or such mixture are mentioned, for example.

[0035] As a reinforcement, clay, talc, a calcium carbonate, zinc carbonate, straw SUTONAITO, a silica, an alumina, a magnesium oxide, a calcium silicate, a sodium aluminate, sodium aluminosilicate, a magnesium silicate, glass balun, carbon black, a zinc oxide, a zeolite, a hydrotalcite, a metal fiber, a metal whisker, a ceramic whisker, a potassium titanate whisker, boron nitride, graphite, a glass fiber, a carbon fiber, etc. are mentioned, for example.

[0036] In the coat agent in this invention, the gas barrier property of the film obtained by carrying out little addition of the cross linking agent component can be raised further.

[0037] As a cross linking agent, an isocyanate compound, a melamine compound, an epoxy compound, a carbodiimide compound, a zirconium salt compound, etc. are mentioned.

[0038] As an agitator, well-known equipments, such as a homogenizer, a ball mill, and high-pressure distribution equipment, can be used that what is necessary is just to carry out by the well-known approach as the preparation approach of coat liquid using the dissolution iron pot equipped with the agitator etc. At this time, the stability of a water solution improves by what the alkali compound is added to the water solution of a polymer (B) for.

[0039] The gas barrier film of this invention is obtained by carrying out stoving, after producing the mixed solution of a polymer (A), a polymer (B), and an inorganic stratified compound (C) and carrying out the coat of this on the surface of a film. Little addition of alcohol or the organic solvent can also be carried out at water for the purpose, such as compaction of the purpose which raises solubility, or a desiccation process, and an improvement of the stability of a solution.

[0040] In order to raise the gas barrier property of a film enough, as for the thickness of the layer in this invention which consists of a polymer (A), a polymer (B), and an inorganic stratified compound (C), it is desirable to make it thicker than at least 0.1 micrometers.

[0041] Moreover, although the polymer concentration at the time of carrying out the coat of the coat agent solution to a film is suitably changed with the viscosity of liquid, or the specification of reactivity and the equipment to be used, it becomes difficult to carry out the coat of the layer of thickness sufficient with a too much thin solution to discover gas barrier property, and it tends to produce the problem of requiring long duration in a subsequent desiccation process. On the other hand, when the concentration of a solution is too high, a problem may be produced in mixed actuation, shelf life, etc. As for such a viewpoint to polymer concentration, it is desirable to make it 10 - 50% of the weight of the range of the whole solution.

[0042] Although especially the approach of coating a film with a solution is not limited, the usual approaches, such as gravure roll coating, reverse roll coating, and wire bar coating, can be used. It may coat, after supplying a tenter type drawing machine, extending and (coincidence biaxial extension) heat-treating a film the transit direction and crosswise at coincidence, after coating an unstretched film first and drying, in order to perform coating in advance of extension, or extending in the transit direction of a film using a multistage hot calender roll etc., and you may extend crosswise by the tenter type drawing machine after desiccation (serially biaxial extension). Moreover, it is also possible to combine extension of the transit direction and the coincidence biaxial extension by the tenter.

[0043] In this invention, in order to carry out crosslinking reaction of the gas barrier layer, it is desirable to heat-treat in an ambient atmosphere 150 degrees C or more preferably the temperature of 120 degrees C or more. If heat treatment temperature is low, crosslinking reaction cannot fully be advanced, and it becomes difficult for the film which has sufficient gas barrier property to obtain. If heat treatment time amount is too short not much, the above-mentioned crosslinking reaction cannot fully be advanced, and it becomes difficult to obtain the film which has sufficient gas barrier property. Usually, 3 seconds or more are preferably good 1 second or more.

[0044]

[Example] Next, an example explains this invention concretely. In this invention, since the gas barrier property of a film changed with the class of base material film, thickness, and the thickness of a coat layer, it evaluated the oxygen transmission coefficient of the coat layer itself. It asked for the oxygen transmission coefficient from the following type.

$1/QF=1/QB+L/PC$, however QF: Oxygen transmittance of a coated film (ml/m² and day-MPa)

QB: Oxygen transmittance of a thermoplastics film (ml/m² and day-MPa)

PC: The oxygen transmission coefficient of a coat layer (ml-mu m/m² and day-MPa)

L: Coat bed depth (micrometer)

Therefore, if PC and L understand the oxygen transmittance of a coated film, it can be estimated from an upper type. Oxygen barrier property measured the oxygen transmittance in 20 degrees C and the ambient atmosphere of 85% of relative humidity with the Mocon oxygen barrier measuring instrument. In addition, the oxygen transmittance of a PET film with a thickness of 12 micrometers made the oxygen

transmittance of 900 ml/m², day-MPa, and a nylon 6 film with a thickness of 15 micrometers 400 ml/m² and day-MPa.

[0045] as example 1 polymer (A) -- made in Unitika Chemical -- polyvinyl alcohol UF040G (whenever [saponification] 99%, average degree of polymerization 400) were dissolved in pure water, and 20% of the weight of the water solution was obtained. It is the equimolar copolymer GANTREZ of the methyl-vinyl-ether-maleic acid made from International Specialty Products as a polymer (B). AN119 was dissolved in the water solution which contains two-mol % of a sodium hydroxide to a carboxyl group, and it ****ed in the solution 20% of the weight. Both water solutions were mixed so that the weight ratio of a polymer (A) and a polymer (B) might become 70/30, then the montmorillonite (Kunimine Industries KUNIPIAF) was added so that it might become 10% of the weight to the solid content total quantity of (A) and (B), and it stirred, and coat liquid was prepared. The coat was carried out by MEIYABA so that the paint film thickness after drying this coat liquid on a biaxial extension PET film (Emblet PET 12 by Unitika, Ltd., thickness of 12 micrometers) might be set to about 2 micrometers, and after drying for 2 minutes at 100 degrees C, it heat-treated for 15 seconds at 200 degrees C. The oxygen transmittance in 20 degrees C of the obtained film and 85%RH showed 26 ml/m² and day-MPa, and the outstanding value.

[0046] The class of an example 2 - 6 inorganic stratified compound (C) and the presentation of a coat agent were changed, and the same actuation as an example 1 was performed. The oxygen transmittance of the obtained film was shown in Table 1.

[0047] Coat liquid was adjusted without adding an inorganic stratified compound (C) in the same procedure as example of comparison 1 example 1. this coat liquid -- an example 1 -- the same -- carrying out -- a PET film -- a coat -- it dried and heat-treated. The oxygen transmittance of the obtained film was 145 ml/m² and day-MPa.

[0048] The outside which does not add either two to example of comparison 3 polymer (A) or a polymer (B) prepared coat liquid in the same procedure as an example 1. this coat liquid -- an example 1 -- the same -- carrying out -- a PET film -- a coat -- it dried and heat-treated. The obtained film dissolved in water on the occasion of a rubbing trial.

[0049] Coating was performed on the conditions shown in Table 1 as example 7 polymer (B) using the isobutylene-maleic-anhydride copolymer (iso van by Kuraray Co., Ltd.). The result was shown in Table 1.

[0050] Example 8 nylon 6 resin was extruded in the shape of a sheet using the extruder (the diameter of 75mm and ratio of length to diameter are the slow compression type monopodium screw of 45) equipped with the T die at the SHINRINDA temperature of 260 degrees C, and the T-die temperature of 270 degrees C, and it was made to stick on the cooling roller adjusted by the skin temperature of 10 degrees C, quenched, and considered as the unstretched film with a thickness of 150 micrometers. Then, the unstretched film was led to the gravure roll type coating machine, it coated so that the coat thickness after drying the coat liquid shown in the example 1 might be set to 2 micrometers, and it dried for 30 seconds in the 80-degree C hot blast dryer. Next, after supplying the film to the tenter type coincidence biaxial drawing machine and carrying out a preheating for 2 seconds at the temperature of 100 degrees C, it extended to the lengthwise direction at 170 degrees C, and extended by one 3.5 times the scale factor of this in 3 times and a longitudinal direction. Next, at 5% of rates of longitudinal direction relaxation, heat treatment for 15 seconds was performed at 200 degrees C, and the biaxial oriented film with a thickness of 15 micrometers was rolled round. The oxygen transmittance of the obtained film and the oxygen transmission coefficient of a coat layer were shown in Table 1. [0051] The coat was carried out to the nylon film like the example 8 using the coat liquid of example 9 example 7. The oxygen transmittance of the obtained film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0052] The coat was carried out to the nylon film like the example 8 except not adding an example of comparison 4 inorganic stratified compound. The oxygen transmittance of the obtained film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0053]

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[Table 1]

		コート剤					基材フィルム	コートフィルム			
		(A)	(B)	(C)	配合比 (重量%) (A)/(B)/(C)	中和 度(当 量%) ^a		コート層 厚み (μm)	コートフィ ルムの酸素 透過度	コート層 の酸素透 過係数	ラビ ング 試験
実 施 例	1	PVA	Gantrez	フニ'7F	70/30/10	2	PET	2.0	26	34	○
	2	PVA	Gantrez	フニ'7F	70/30/20	2	PET	2.0	8	16	○
	3	PVA	Gantrez	フニ'7F	70/30/1	2	PET	2.0	101	228	○
	4	PVA	Gantrez	ルセタイト	70/30/1	2	PET	2.0	93	207	○
	5	PVA	Gantrez	ソマシフ	70/30/1	2	PET	2.1	93	223	○
	6	PVA	Gantrez	フニ'7F	90/10/10	0	PET	1.9	13	23	○
	7	PVA	4/n'7	フニ'7F	70/30/10	60	PET	2.0	43	90	○
	8	PVA	Gantrez	フニ'7F	70/30/10	2	Nylon	1.1	108	163	○
	9	PVA	4/n'7	フニ'7F	70/30/10	60	Nylon	1.1	93	133	○
比 較 例	1	PVA	Gantrez	なし	70/30/0	2	PET	2.0	145	346	○
	2	PVA	なし	フニ'7F	100/0/5	0	PET	2.0	67	145	×
	3	なし	Gantrez	フニ'7F	0/100/5	2	PET	2.0	217	372	×
	4	PVA	Gantrez	なし	70/30/0	2	Nylon	1.1	270	914	○

* (B) がイソパンの場合は NH_4OH により中和。(B) がGantrezの場合は NaOH により中和。

(c) の層状化合物は、

ルーセントタイト : コープケミカル社製 合成スメクタイト

ソマシフ : コープケミカル社製 膨潤性合成フッ素雲母

[0054]

[Effect of the Invention] By making the coat agent of this invention form in the front face of a thermoplastics film, the gas barrier property which could manufacture the film which has the outstanding gas barrier property ability, and was excellent also in the bottom of high humidity can be held.

[Translation done.]